THERMAL CRACKING OF LOW-TEMPERATURE LIGNITE PITCH

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INTRODUCTION

The tar used in this study was produced by the Texas Power & Light Company from a Texas lignite carbonized at about 500° C in a fluidized bed. The pitch, as used in this research program, is the tar distillation residue boiling above 350° C. This pitch is about 40 to 50 percent of the crude tar. Pitch is a complex resinous mass of polymerized and polycondensed compounds (1). It is an amorphous solid material and quite brittle at room temperature. The pitch analyses average 84 percent carbon, 8 percent hydrogen, 5 percent oxygen, and 1 percent each of nitrogen and sulfur. It is chemically similar to the tar from which it is prepared, being mainly mixtures of the higher homologs of the compounds contained in the distillable fractions of the tar.

The pitch is potentially useful as a binder in the manufacture of products such as roofing cement, metallurgical electrodes, asphalt paving, and pitch fibre pipe, if its characteristics can be modified by physical and chemical techniques to approximate those of asphalt and bituminous binders (3).

Researchers of the Bureau of Mines, U. S. Department of the Interior, have investigated three methods for changing the lignite pitch characteristics.

Air-blowing, which is used successfully to treat bituminous pitch by lowering the hydrogen content and increasing the softening point and the penetrability, was not too effective with lignite pitch (1, 2).

Catalytic dehydrogenation (6) was found to be effective in reducing the hydrogen content of the pitch, but catalyst cost per pound of treated pitch is high, and the catalyst recovery cost would be prohibitive.

Thermal cracking has proven to be the most effective in changing the pitch characteristics. This report covers the preliminary work done on thermal cracking of pitch and shows the variety of products that may be obtained.

Thermal cracking is widely used in the petroleum industry, particularly for the production of olefins. Thermal cracking has also been used in the treatment of coal tar (4, 5), but seldom has been used in the treatment of pitch. The successful treatment of pitch by this process could upgrade the pitch into metallurgical coke, binders, oxidation feedstock for phthalic and maleic anhydrides, and gases such as hydrogen, methane, and ethylene.

The binding ability of the cracked pitch and oil distillation pitch can be determined by the quality of metallurgical electrodes produced using the pitches as binders. Many factors affect the binding properties of the materials being used as binders, with different producers and consumers using entirely different standards, so the electrode quality tests were used to help evaluate the effectiveness of thermal cracking of the lignite pitch.

EQUIPMENT

The thermal cracking system is shown in figures 1 and 2. The feed tank (figure 2, A) is made from a 13-in. length of 10-in. diameter schedule 40 pipe, to which a cone has been added for the bottom. The tank is heated by commercial electric heaters. The feed pump (B) is a small gear pump with a variable speed drive. The thermocracker (D) is a 4-1/2 ft-length of 2-1/2-in. diameter schedule 40, type 304, stainless-steel pipe, heated by external electric heaters. The heaters are controlled by outside surface thermocouples welded to the reactor. The receiver (E) is a 20-in. length of 4-in. diameter schedule 40 pipe. The receiver is flanged so that it can be bolted to the bottom of the reactor. The condenser (F) is a 30-in. length of 6-in. diameter pipe, swaged at the bottom end to 1-in. diameter and flanged at the top. The top flange supports a water-cooled tube which inserts into the condenser body in the manner of a cold finger. The knockout (G) is a 34-in. length of a 2-in. diameter pipe having a tangential gas inlet about 8-in. from the bottom. The scrubber (H) is a 30-in. length of a 4-in. diameter pipe having a water-spray nozzle near the top. The water from the scrubber drains into a standpipe water-seal tank (I). The water-seal tank is a piece of 6-in. diameter pipe. The gas meter (J) is a laboratory-type wet-test meter capable of metering 1,000 cu ft of gas at standard conditions.

PROCEDURE

Lignite pitch at 200° C was pumped from the feed tank through electrically heated lines into the top of the thermocracker. The temperature of the thermocracker was maintained at approximately 790° C as indicated by the outside surface thermocouples. At the end of a run, the flow of pitch was stopped and the pump was flushed with a low-boiling tar fraction to keep the impeller of the pump from freezing. Reactions within the cracker produced coke, cracked pitch, oil, and gas. Both the top and bottom of the cracker were removed, and coke was removed from the sides and weighed. Cracked pitch caught in the receiver was weighed and analyzed. The oil removed by the condenser and knockout chamber was weighed and then distilled to 400° C, leaving a pitch residue. This pitch residue was analyzed and, if found to have the desired carbon-to-hydrogen atomic ratio (1.20 to 1.80), was used as a binder for electrodes. Distillate from the oil may be oxidized to phthalic and maleic anhydrides or separated into acids, bases, and neutral oils. Gas from the cracker was cooled and scrubbed, then metered, sampled, and analyzed by gas chromatography.

RESULTS AND DISCUSSION

Results of the thermal cracking tests are given in tables 1 to 4. Of the four major products obtained from the pitch--coke, cracked pitch, oil, and gas--the coke averaged about 15 to 25 percent of the feed to the cracker, the cracked pitch amounted to about 20 to 40 percent, the oil was about 20 to 30 percent, while the balance of the feed to the cracker consisted of gas.

Distribution and yield rates of products (figures 3 to 6) are as expected considering the reaction within the cracker at different crude pitch feed rates. As the pitch is heated it begins to vaporize, and the turbulence of the vapors splashes some of the fluid onto the hot wall where it sticks and is coked. If enough heat is available, the rest of the pitch is vaporized and cracked. As the cracked materials leave the hot zone, heavy high-boiling materials condense immediately and collect in the receiver as cracked pitch; the oil and gas vapors pass on to the condenser. If there is not enough heat available to vaporize all of the pitch fed to the cracker, the unvaporized portion flows through the hot zone and into the receiver without being completely cracked. Such is the case when the crude pitch feed rate is high, the residence time in the cracker being shorter and less time being available for heat to penetrate the interior of the pitch mass. High crude pitch rates also lower the temperature inside the cracker, reducing the amount of coke formed.

Figures 3 and 4 appear to reflect these effects. The coke rate increases more slowly and the cracked pitch rate increases more rapidly than does the crude pitch feed rate. Since the gases are formed by several reactions, each related to the degree of cracking and coking, the gas production rate decreases with the increase in crude pitch feed rate (figure 5). Gases are produced by coking of pitch adhering to the cracker wall, then these gases are cracked to produce hydrogen and olefins. In addition to gas produced from coke, other gases are produced by devolatilization and thermal cracking of the pitch and are also subjected to further cracking. A significant amount of ethylene was produced in the cracker.

Oil produced in the cracker, upon distillation, yielded a pitch residue potentially useful as electrode binder, paving material, pitch fibre pipe, or roofing material, along with a distillate that can be further treated to give valuable chemical intermediates. Table 3 gives characteristics of the pitch residue and some preliminary data on electrodes made with the pitch as binder. The decrease in carbon-to-hydrogen atomic ratio of the pitch residue in relation to the crude pitch feed rate (figure 7) again reflects the inhibition of cracking by relatively high crude pitch feed rates.

The oil is produced in two ways--by cracking of the pitch, the most desirable method, and by devolatilization of pitch without cracking. This is the reason why the oil production rate can increase approximately in proportion to the crude pitch feed rate (figure 6). However, the quality of the oil decreases with decrease in degree of cracking, as is shown by the drop in the carbon-to-hydrogen atomic ratio.

CONCLUSIONS

Thermal cracking of low-temperature lignite tar pitch converted the pitch into a material that served as a satisfactory binder in the manufacture of carbon electrodes. Compressive strength and electrical resistivity of the resulting electrodes fell within acceptable ranges. Crude pitch feed rate to the thermocracker significantly affected the rate of formation of products and the composition of the pitch residue from distillation of oil produced in the cracker.

REFERENCES

1. Berber, John S., and Richard L. Rice. Oxidation of a Low-Temperature Lignite Tar Pitch. Preprints, Div. of Fuel Chemistry, Am. Chem. Soc., v. 8, No. 3, Aug. 31-Sept. 3, 1964, pp. 145-151.

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TABLE 1. - Gas products from thermal cracking of low-temperature lignite tar pitch

Run no.	Crude pitch rate, pph	Gas rate, scfh	Constituents in gas, pct								
			N_2	O_2	CO_2	CO	H_2	CH_4	C_2H_6	C_2H_4	C_3 +
35	2.0	16.7	49.35	0.76	0.45	4.12	21.99	19.67	0.44	2.37	0.85
37	6.0	37.0	8.77	.15	.96	8.38	15.80	42.19	4.30	14.05	5.40
38	9.0	45.2	5.06	.09	.81	7.29	22.63	37.32	4.98	12.63	9.19
43	10.0	51.3	8.35	.09	.80	7.40	20.08	37.94	4.64	12.78	8.12
40	11.0	51.4	1.13	.21	.80	7.49	37.96	35.74	2.64	11.53	2.50
30	13.1	55.1	1.17	.14	.83	7.91	30.52	41.33	3.73	12.08	2.29
42	17.0	66.6	9.84	.08	1.28	7.42	19.96	36.18	5.04	12.76	7.44
41	21.0	76.2	17.28	.13	.92	6.82	14.02	34.88	4.44	14.76	6.75

TABLE 2. - Coke, pitch, and oil products from thermal cracking of low-temperature lignite tar pitch

Run no.	Feed rate, pph	Coke rate, pph	Cracked pitch rate, pph	Oil rate, pph	Distillate from oil, wt pct	Anhydrides from distillate, wt pct			Composition of distillate, vol pct		
						PAA[1]	MAA[2]	Total	Acids	Bases	Neutral oil
35	2.0	0.8	0.2	0.8	40.3	16.4	14.5	30.9	10.5	6.0	83.5
37	6.0	1.4	1.4	1.4	27.2	17.0	14.4	31.4	10.0	8.0	82.0
38	9.0	2.0	2.0	2.2	29.1	11.7	15.2	26.9	10.0	7.0	83.0
43	10.0	2.0	3.6	2.6	34.4	10.1	13.9	24.0	13.5	5.0	81.5
40	11.0	2.2	3.2	3.6	32.6	11.0	12.8	23.8	15.0	5.0	80.0
30	13.1	2.4	3.3	4.1	27.8	14.3	13.8	28.1	----	---	----
42	17.0	3.0	6.2	5.6	25.9	10.6	14.4	25.0	12.5	4.0	83.5
41	21.0	3.8	13.4	7.2	25.9	8.0	12.9	20.9	15.0	5.0	80.0

1/ Phthalic anhydride.
2/ Maleic anhydride.

TABLE 3. - Characteristics of pitch and electrodes

Run no.	Crude pitch rate, pph	Oil, wt pct	Pitch from oil, wt pct	Properties of pitch				Properties of electrodes		
				Carbon, wt pct	Hydrogen, wt pct	C/H ratio	Softening point, °C	Coke type	Strength, kg/cm^2	Resistivity, ohm-cm
35	2.0	40.0	56.6	85.63	5.60	1.27	110			
37	6.0	23.3	71.0	88.86	4.69	1.58	145			
38	9.0	24.4	68.5	85.55	5.84	1.22	100	Lignite 1/	183	0.0220
43	10.0	26.0	62.9	85.67	6.00	1.19	115	Petroleum	242	.0076
40	11.0	32.7	66.3	85.60	5.90	1.21	104	Lignite 2/	355	.0180
30	13.1	31.3	68.3	85.81	6.37	1.46	116	Petroleum	323	.0074
42	17.0	32.9	72.6	82.12	7.51	.91	65			
41	21.0	34.3	72.6	81.90	7.57	.90	65			

1/ Uncalcined lignite pitch coke.
2/. Calcined lignite pitch coke.

TABLE 4. - Material balance for thermal cracking of low-temperature lignite pitch

Run no.	Crude pitch rate, pph	Coke rate, pph	Cracked pitch rate, pph	Oil rate, pph	Gas rate, pph	Total, pph	Gain or loss, pph	Recovery, pct
35	2.0	0.8	0.2	0.8	0.9	2.7	+ 0.7	35.0
37	6.0	1.4	1.4	1.4	1.9	6.1	+ .1	1.7
38	9.0	2.0	2.0	2.2	2.2	8.4	- .6	6.7
43	10.0	2.0	3.6	2.6	2.6	10.8	+ .8	8.0
40	11.0	2.2	3.2	3.6	1.9	10.9	- .1	.9
30	13.1	2.4	3.3	4.1	2.2	12.0	- 1.1	8.4
42	17.0	3.0	6.2	5.6	3.4	18.2	+ 1.2	7.1
41	21.0	3.8	13.4	7.2	4.2	28.6	+ 7.6	36.2

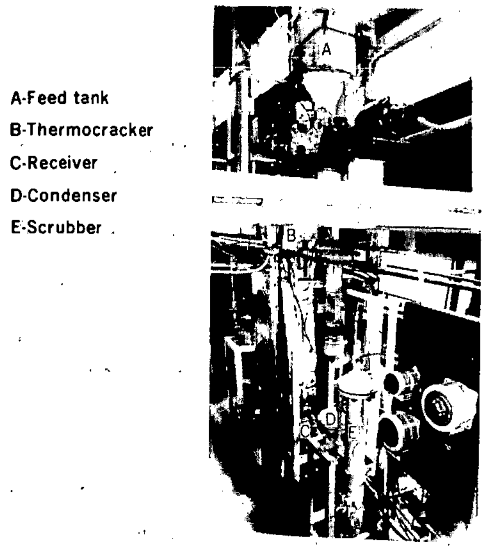

FIGURE 1. - Pitch Thermal Cracking Apparatus.

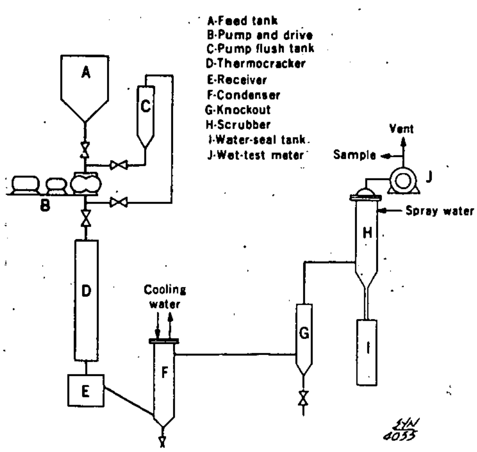

FIGURE 2. - Thermal Cracking System.

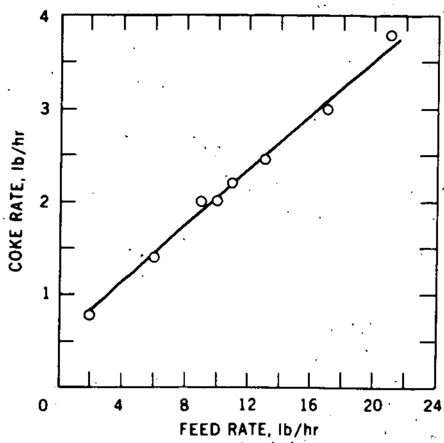

FIGURE 3. - Coke Rate Based on Crude Pitch Feed Rate - Thermal Cracking.

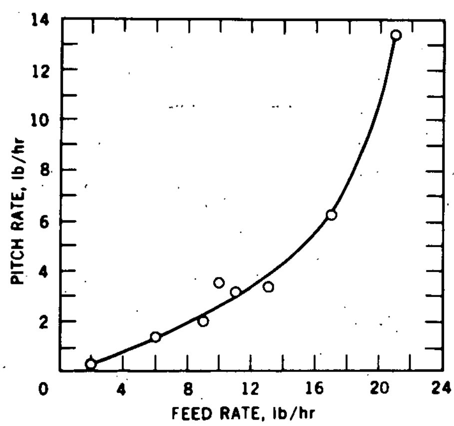

FIGURE 4. - Product Pitch Rate Based on Crude Pitch Feed Rate - Thermal Cracking.

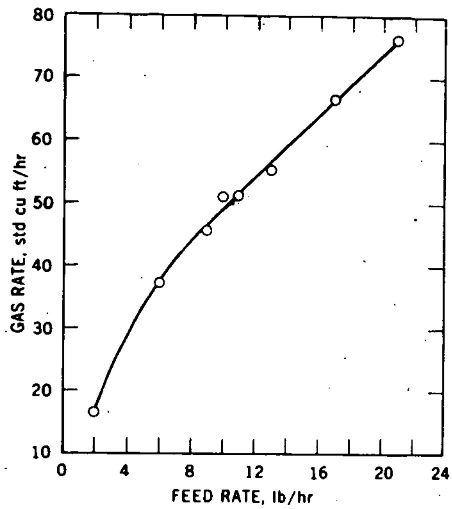

FIGURE 5. - Gas Production Rate Based on Crude Pitch Feed Rate - Thermal Cracking.

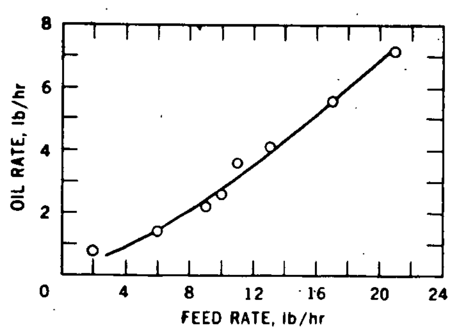

FIGURE 6. - Oil Rate Based on Crude Pitch Feed Rate - Thermal Cracking.

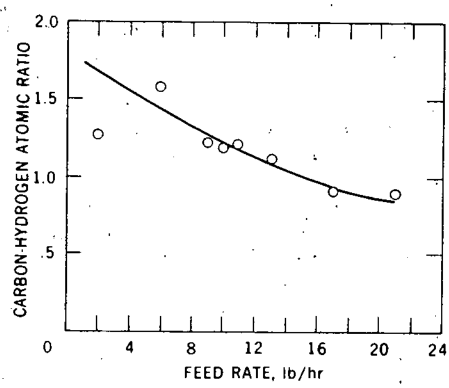

FIGURE 7. - Carbon-to-Hydrogen Atomic Ratio of Oil Distillation Residue Based on Crude Pitch Feed Rate.